Supporting Information

Anthracene extended viologen-incorporated ionic porous organic polymer for efficient aerobic photocatalysis and antibacterial activity

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1. Materials characterizations and Experimental Section

1.1 Materials characterizations

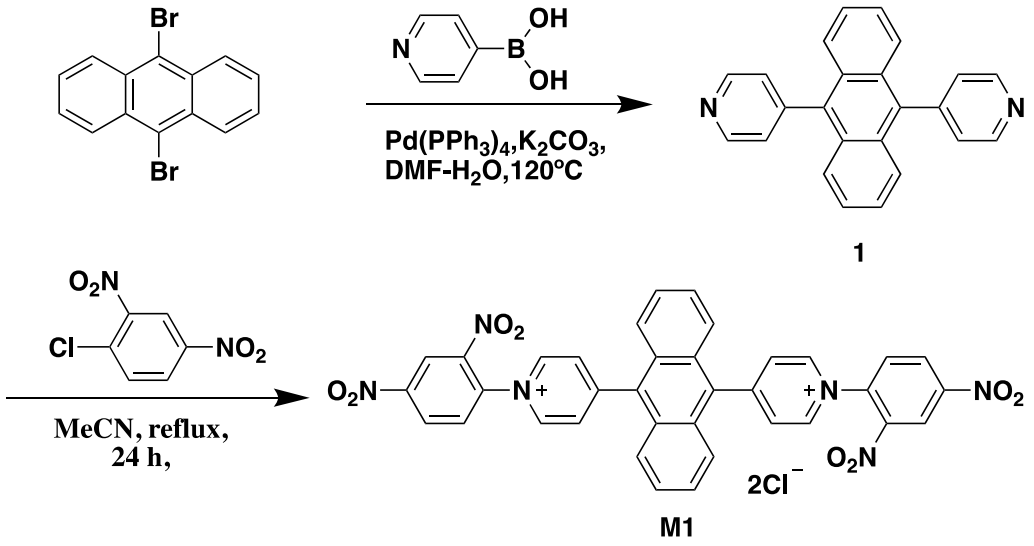
^{1}H NMR spectra were recorded using a Bruker Avance II 400 instrument with CD_3OD、DMSO-d_6 and $CDCl_3$ as solvents. ^{13}C NMR spectra were recorded on a Bruker Av500 NMR spectrometer at 126 MHz. All chemical shifts are given in parts per million (ppm) relative to tetramethylsilane (TMS). Fourier transform infrared spectra (FTIR) analysis was carried out on a JASCO IR-4100 spectrometer and use the traditional KBr plate method; tested in the range of 400-4000 cm^{-1}. High-resolution mass spectra (HRMS) were recorded on a Agilent G6224A-TOF mass spectrometer. Solid-state ^{13}C CP/MAS (cross-polarization with magic angle spinning) spectra were carried out on an Agilent DD2-500MHz nuclear magnetic resonance spectrometer. UV-Vis studies were recorded on a Hitachi UV-4100 spectrometer. All UV-Vis spectra were carried out at room temperature. X-ray diffractions (XRD) measurements were recorded from 2° to 40° on a Rigku D/max-2400 diffractometer (40 kV, 200 mA) with a copper target at a scanning rate of 2° min^{-1}. Adsorption and desorption data of gases were collected on a Quantachrome Autosorb iQ analyzer. Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/DSC 3+ thermal analyzer under an atmosphere of flowing N_2. The samples were heated from room temperature to 800 °C at a heating rate of 10 °C min^{-1}.

Antibacterial Experiment: To evaluate the antibacterial activities of the AN-POP and BD-POP samples, the inhibition zones, and bactericidal efficiency were performed. For inhibition zones, the samples were placed in agar plates which were inoculated by 10^6 colony forming units per mL (CFU mL^{-1}) bacteria liquid, and then incubated in bacteriological incubator at 37 °C for 24 h. The image of the inhibition zone was obtained with the iPhone 6s plus (Apple, 12-megapixel camera, *ƒ*/2.2 aperture). As for bactericidal efficiency, the live or dead bacteria staining was utilized after 12 h of incubation using acridine orange (AO)-propidium iodide (PI) double fluorescent staining and then the bacteria which attached to the surfaces were observed by fluorescence microscopy (Olympus, BX-51). Cell Culture: Raw and LSEC cells were both grown in high-glucose DMEM media supplemented with 10% fetal bovine serum (FBS), 100 μg/mL streptomycin, and 100 U/mL penicillin.

1.2. Materials

All the chemicals were purchased from commercial suppliers and used without further purification unless mentioned. Other solvents, such as chloroform, tetrahydrofuran and toluene were used as received. **TAPT** was prepared according to previously reported procedure[1].

1.2.1 The syntheses of monomer **M1**[2], and **M2**[3].



Monomer **1**: To a mixture of 4-pyridylboronic acid (0.615 g, 5 mmol), 9,10-dibromoanthracene (0.672 g, 2 mmol) and $Pd(PPh_3)_4$ (231 mg, 0.2 mmol) in DMF (80 mL) purged with Ar was added dropwise a solution of K_2CO_3 (2.72 g, 20 mmol) in H_2O (10 mL). After being stirred at 100 ^oC for 18 h, the mixture was cooled to room temperature and removed the aqueous phase. And the residue was redissolve in a mixture of chloroform and water. The two phases were separated, and the organic layer was washed twice with water. Finally, to the last portion of water (80 mL), hydrochloric acid (1 M) was added until pH =1. During acidification, some of the residue dissolved in the water phase, which gave a yellow color. The organic phase was removed and discarded. To the aqueous phase was added potassium hydroxide (1 M solution) until pH = 8. The product was then isolated by extraction into chloroform (2× 80 mL) and evaporation of the solvent. The procedure of acidification extraction-neutralization was repeated until the product was pure. ^1H NMR (400 MHz, CDCl3, **Fig.S1**) δ 8.89 (d, J = 4.2 Hz, 4H), 7.64 (dd, J = 3.3 Hz, 4 H), 7.47 (d, J = 4.2 Hz, 4H), 7.42 (dd, 3.3 Hz, 6.8 Hz, 4H);

Monomer **M1**: 9,10-bis(3-pyridyl)anthracene (531.2 mg, 1.6mmol) and 1-chloro-2,4-

dinitrobenzene (1.135 g, 5.6 mmol) were dissolved in MeCN (17.5 mL). Nitrogen was bubbled through the solution for 5 min. After that, the reaction mixture was stirred in the oil bath pot for 72 hours with the temperature preserved at 90 °C. The final suspension was filtered and subsequently washed with MeCN and diethyl ether. The resulting powder was dried under vacuum for 12 h to yield (**M1**, 1.05 g, 63%).^{1}H NMR (400 MHz, Methanol-d4, **Fig.S2**) δ 9.60 (d, J = 6.2 Hz, 2H), 9.40 (s, 1H), 9.05 (d, J = 10.4 Hz, 1H), 8.84 (d, J = 5.3 Hz, 2H), 8.62 (dd, J = 17.8, 7.5 Hz, 4H), 7.94 (s, 2H), 7.74 (s, 4H), 7.58 (d, J = 4.3 Hz, 4H), 7.44 (d, J = 10.0 Hz, 2H).

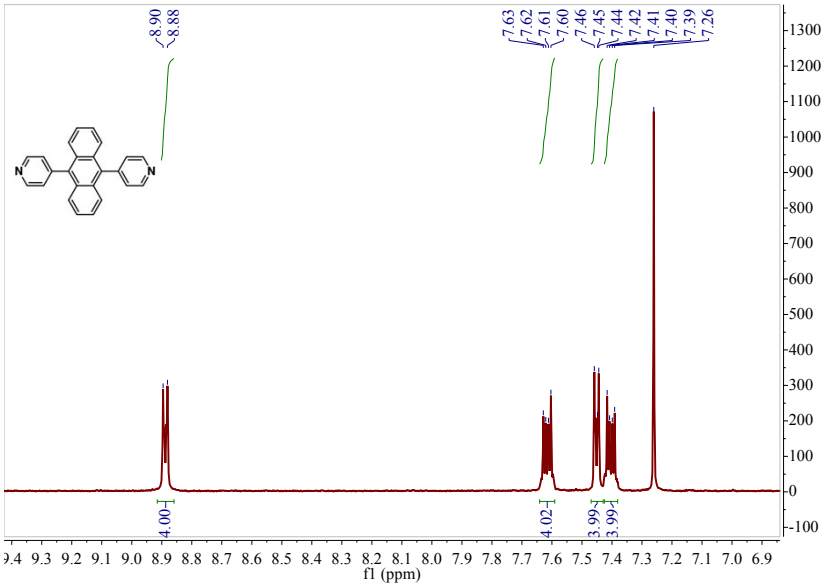


Fig. S1 ^{1}H NMR spectrum of monomer **1**.

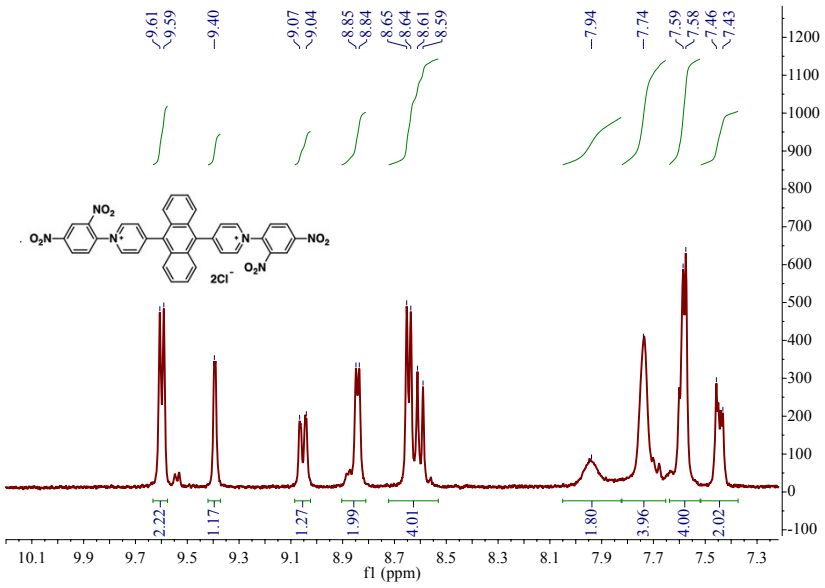
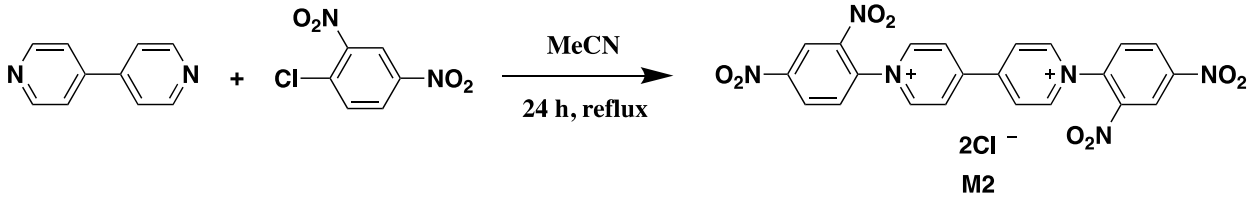


Fig. S2 ^{1}H NMR spectrum of monomer **M1**.



Monomer **M2**: 4,4‘-Bipyridine 4 g (25.6 mmol) and 26 g (89,6 mmol) of 2,4-dinitro-chlorobenzene in MeCN (150 mL) were stirred at 90°C for 24 h under reflux. At the beginning, the solution was clear brown, after 4 h first yellow crystals precipitated. The yellow suspension was filtered. The filtrate was washed once with MeCN (50 mL) and four times with diethyl ether (40 mL),and dried for 16 h in vacuum (yield: 19 mmol, 74%).^{1}H NMR (400 MHz, Methanol-d_4 **Fig. S3**) δ 9.67 (s, 4H), 9.34 (s, 4H), 9.11 (d, J = 3.1 Hz, 4H), 8.99 (d, J = 9.4 Hz, 4H), 8.41 (d, J = 7.9 Hz, 4H). ^{13}C NMR (126 MHz, Methanol-d_4, **Fig. S4**) δ 155.11, 147.23, 143.39, 140.77, 139.48, 135.99, 134.84, 128.82, 127.29, 122.61, 119.26.

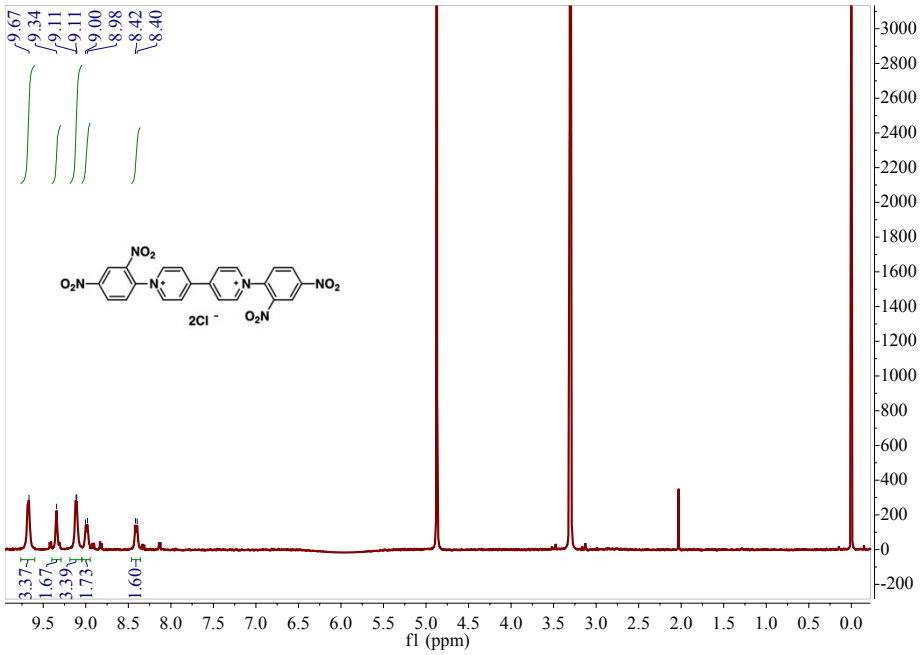


Fig. S3 ^{1}H NMR spectrum of monomer **M2**.

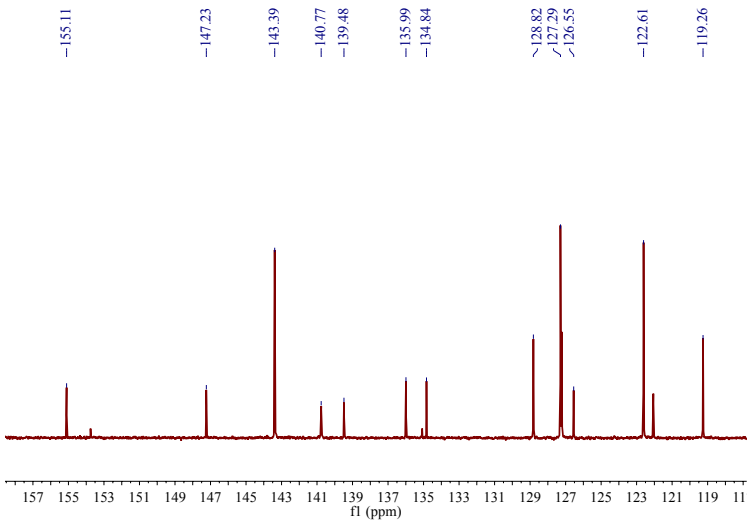


Fig. S4 ^{13}C NMR spectrum of monomer **M2**

1.2.2 The syntheses of polymer **AN-POP-1** and **BD-POP** .[4]

TAPT (0.177 g, 0.5 mmol) and **M1** 0.318g (0.5 mmol), or **M2** were mixed in a 4:1 EtOH: H_2O solvent and degassed in a Schlenk tube via three freeze-pump-thaw cycles. After that, the reaction mixture was stirred in the oil bath pot for 72 hours with the temperature preserved at 120 °C. After the reaction completed, the reaction mixture was filtered. The solid was washed several times with ethanol and water. Finally, the crude product was extracted with methanol in a Soxhlet apparatus for 48 h and dried at 120 °C under vacuum overnight to give **AN-POP-1** (50%) as red solids, **B-POP** as orange solids (54%), and **BD-POP** as dark brown solids (60%).

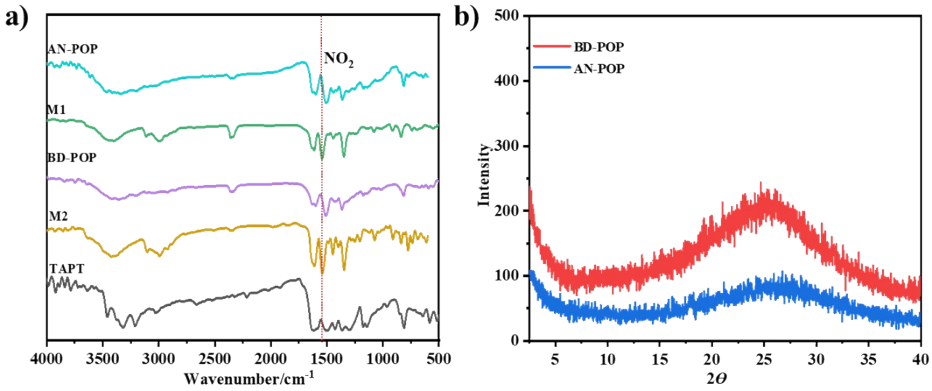


Fig. S5 a) FT-IR spectra of M1, M2, TAPT, **BD-POP** and **AN-POP**; b) PXRD of polymer **BD-POP** and **AN-POP**, respectively.

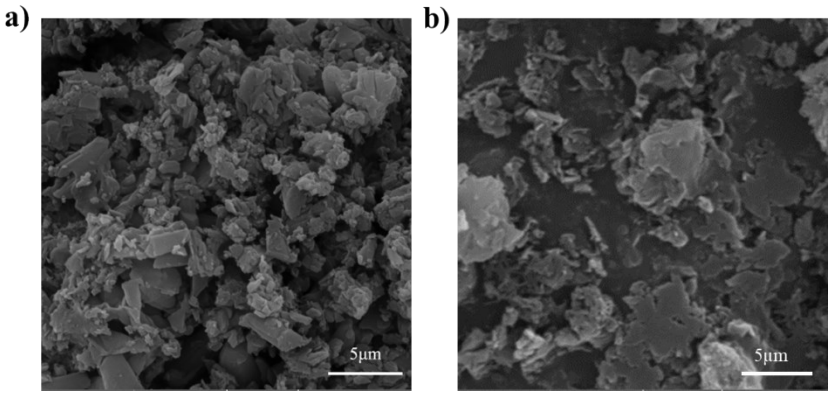


Fig. S6 SEM images of polymer **a) BD-POP** and **b) AN-POP**, respectively.

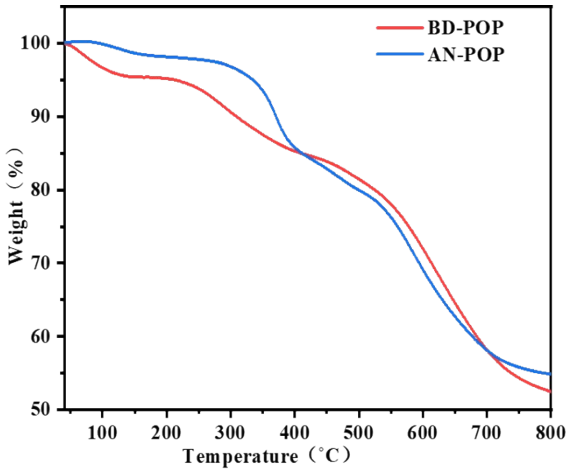


Fig. S7 TGA curve of polymer polymer **BD-POP** and **AN-POP**, respectively.

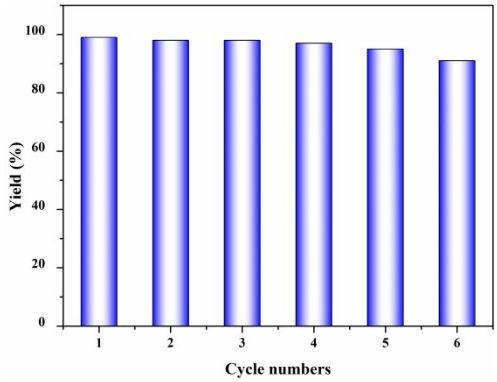


Fig. S8 Cycling performances of **AN-POP** for the oxidative coupling of benzylamine.

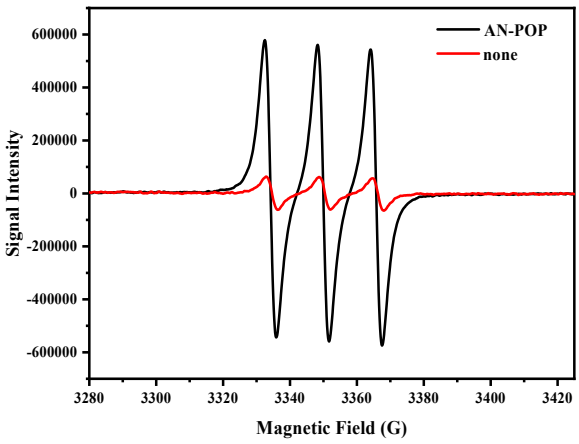
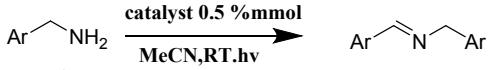


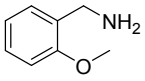
Fig. S9 The EPR spectra of **AN-POP** in the presence of air and TEMP after visible light irradiation.

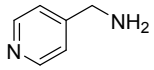
Table S1 Photocatalytic oxidative coupling of amines into imines by **AN-POP**

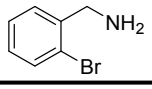


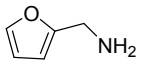
1 **2**

1A:Ar=C_6H_5
1B:Ar=4F-C_6H_4
1C:Ar=4Cl-C_6H_4
1D:Ar=4MeO-C_6H_4
1F:Ar=$_4$Me-C_6H_4

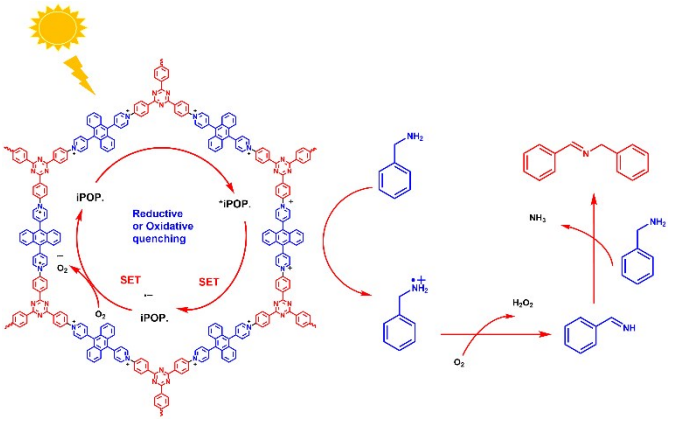
1E: 

1H: 

1G: 

1I: 

Entry	substrate	t(h)	Conversion/%	Selectivity/%
1	1A	24	>99	>95
2	1B	24	>99	>96
3	1C	24	>99	>98
4	1D	24	>98	>94
5	1E	24	>99	>99
6	1F	24	>99	>95
7	1G	24	>99	>99
8	1H	24	>97	>91
9	1I	24	>99	>97



Scheme S1 Proposed reaction mechanism for the oxidative coupling of benzylamine photocatalyzed by **AN-POP**.

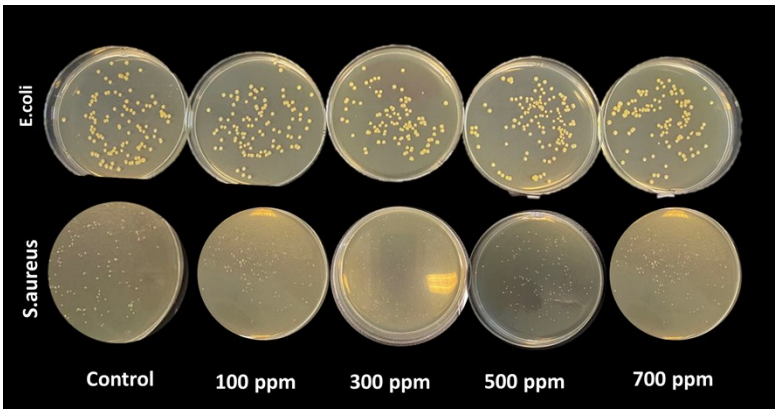


Fig. S10 Photo of colony growths after sterilization of S. aureus and E.coli with different concentrations of polymers (**BD-POP**).

Control experiment:

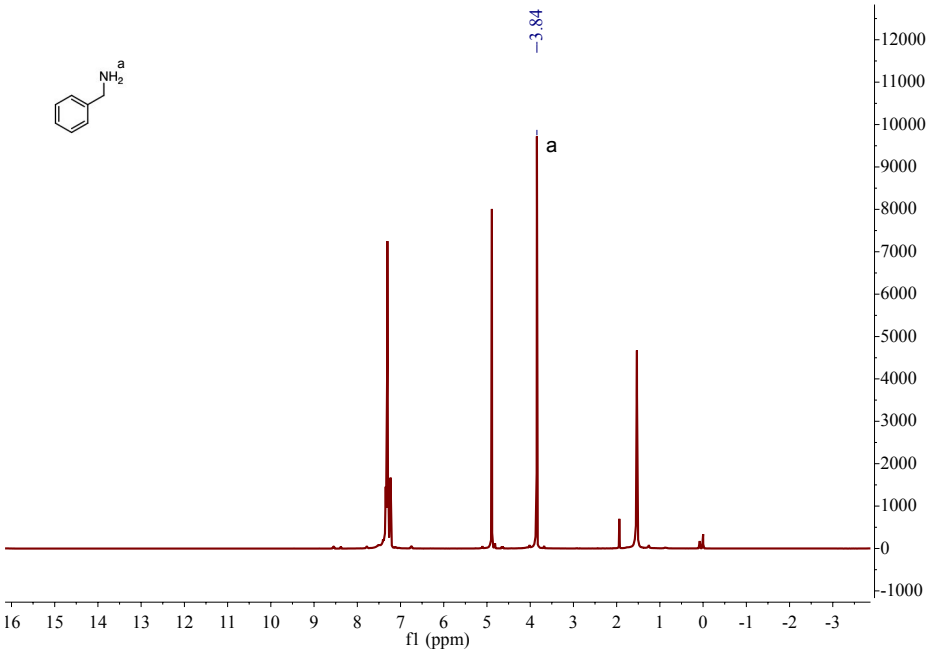


Fig. S11 ^{1}H NMR spectrum of the reaction mixture in the dark (Entry 1, Table 1).

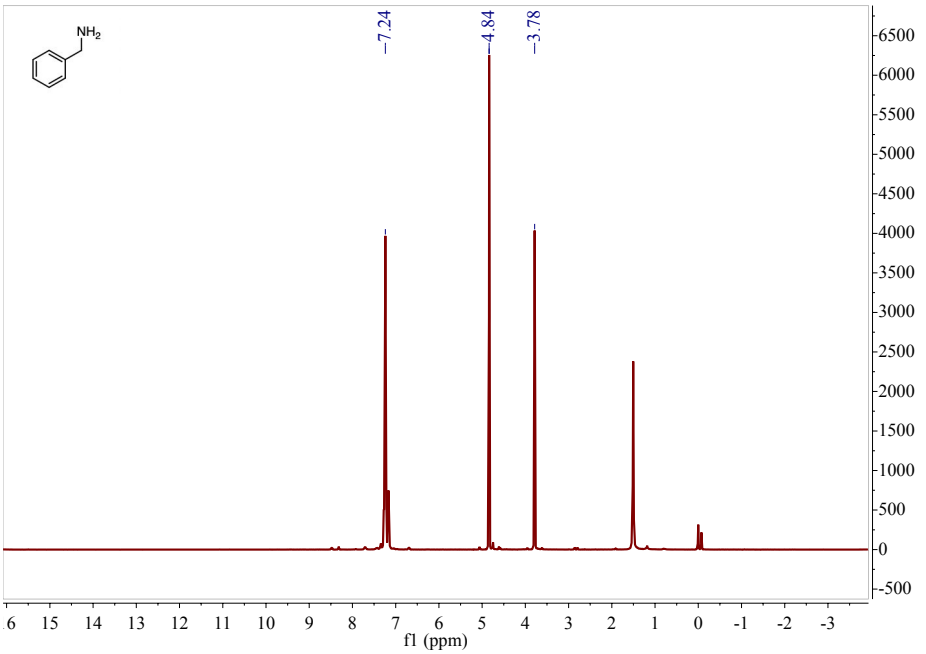


Fig. S12 ^{1}H NMR spectrum of the reaction mixture reaction mixture under argon atmosphere (Entry 2, **Table 1**)

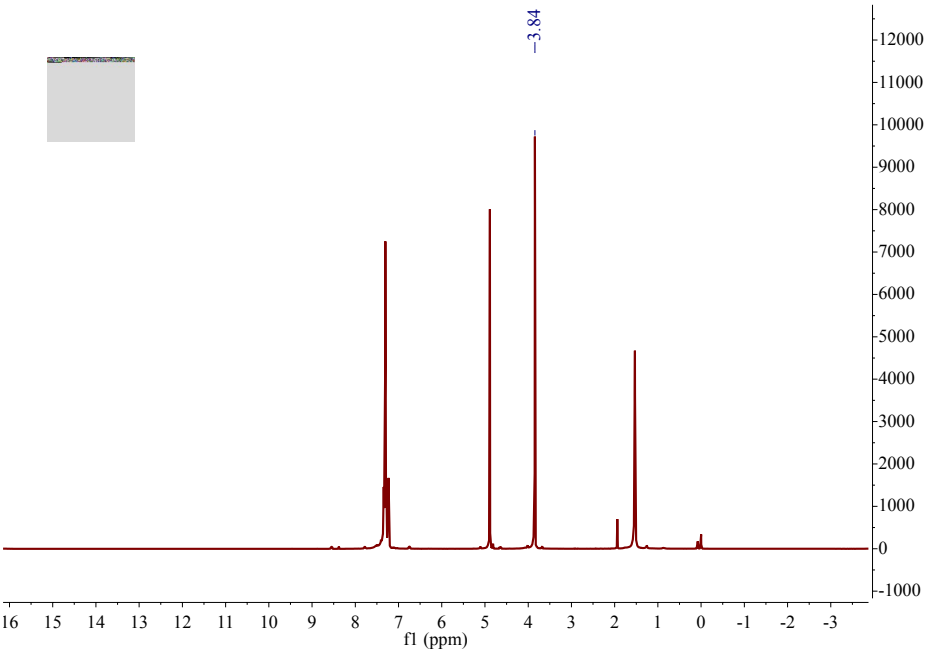


Fig. S13 ^{1}H NMR spectrum of the reaction mixture without photocatalyst (Entry 3, Table 1).

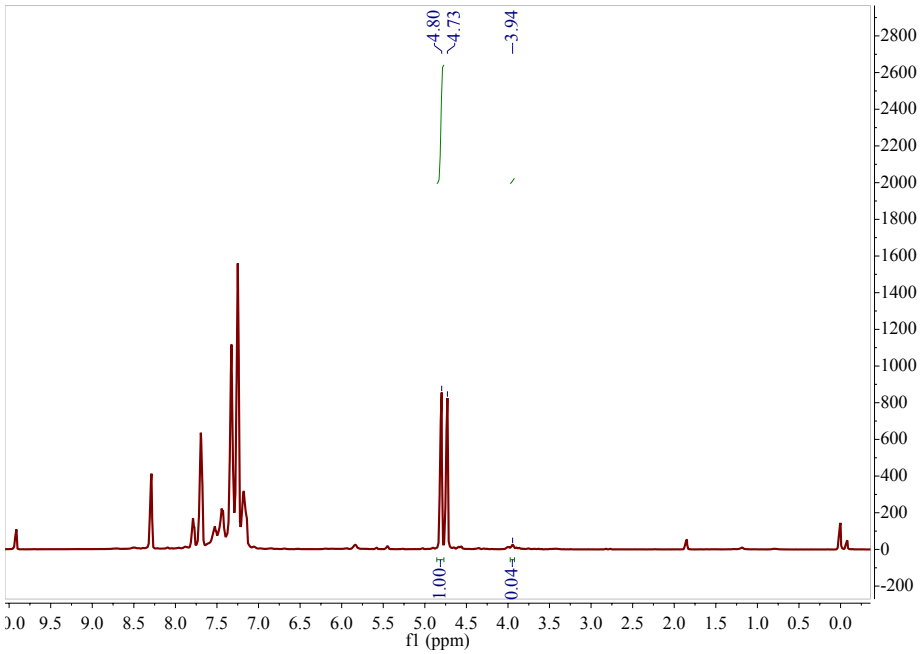


Fig. S14 ^{1}H NMR spectrum of the reaction mixture in presence of NaN_3 (Entry 5, Table 1).

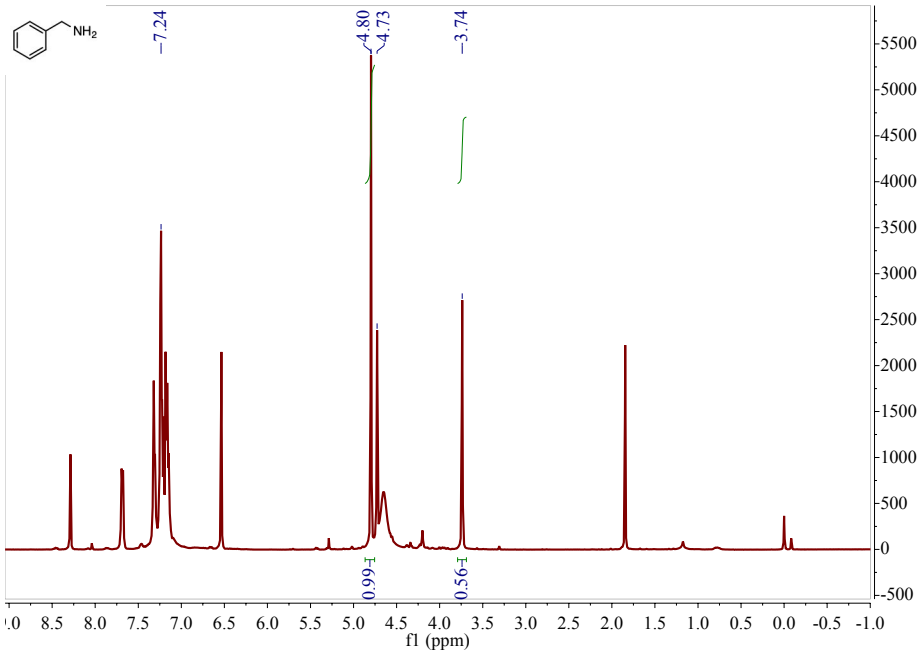


Fig. S15 ^{1}H NMR spectrum of the reaction mixture in presence of BQ (Entry 6, Table 1).

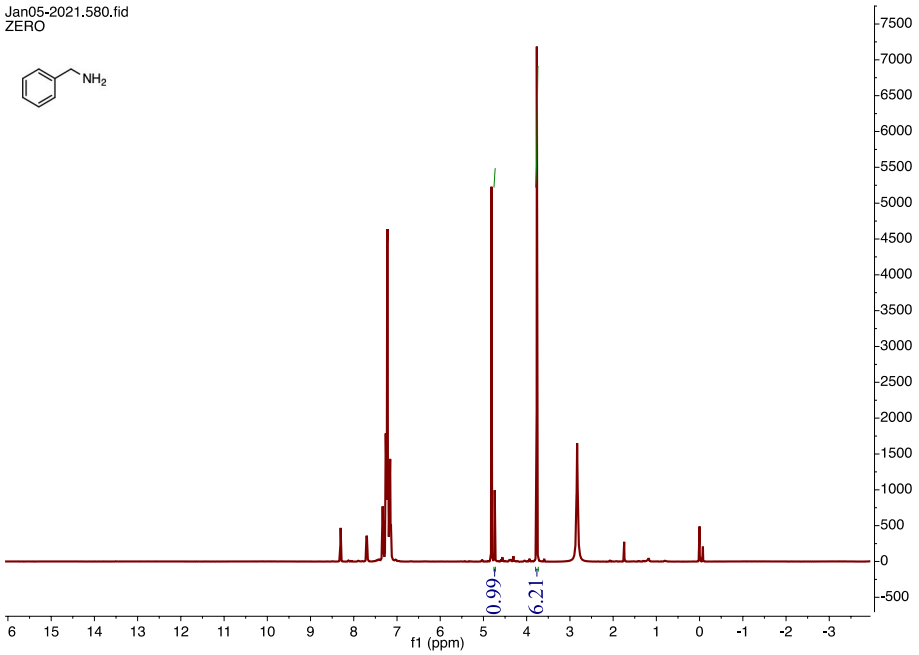


Fig. S16 ^{1}H NMR spectrum of the reaction mixture in presence of **BD-POP** (Entry 7, Table 1).

Ref:

[1] D. Mullangi, D. Chakraborty, A. Pradeep, V. Koshti, C. P. Vinod, S. Panja, S. Nair, R. Vaidhyanathan, *Small,* 2018, 14, 1801233.
[2] S. Asafte, E. D. Clercq, J. Med. Chem. 2010, 53, 9, 3480–3488
[3] W. Fudickar, T. Linker, J. Org. Chem. 2017, 82, 9258−9262
[4] G. Das, T. Skorjanc, S.K. Sharma, et al, J. Am. Chem. Soc., 2017, 139, 9558−9565.